

## INTER-DIFFUSION IN THE PRESENCE OF FREE CONVECTION

*Prabhat K. Gupta*

Department of Materials Science & Engineering

The Ohio State University

2041 College Road

Columbus, OH 43210

email: gupta.3@osu.edu

550-29

08-1-97

NAG8-1470

(Microgravity Materials Science Conference, July 1998)

### *Abstract*

Because of their technological importance, establishment of the precise values of interdiffusion coefficients is important in multicomponent fluid systems. Such values are not available because diffusion is influenced by free convection due to compositionally induced density variations. In this project, earth based diffusion experiments are being performed in a viscous fluid system PbO-SiO<sub>2</sub> at temperatures between 500-1000 C. This system is chosen because it shows a large variation in density with small changes in composition and is expected to show a large free convection effect. Infinite diffusion couples at different temperatures and times are being studied with different orientations with respect to gravity. Composition fields will be measured using an Electron Microprobe Analyzer and will be compared with the results of a complementary modeling study to extract the values of the true diffusion coefficient from the measured diffusion profiles.

### *Introduction:*

Interdiffusion describes the evolution of compositional inhomogeneities in systems containing more than one component. Since most material systems of technological importance are not single component and since interdiffusion is the rate controlling step in most processing operations involving compositional changes (e.g., crystal growth, melting, dissolution, precipitation, and sintering), establishment of precise values of interdiffusion coefficients and of their variations with respect to composition and temperature is of much interest. While techniques for measuring interdiffusion coefficients are available, values of interdiffusion coefficients in liquids (and supercooled liquids) are available only for a few systems and that too with limited precision. One of the reasons is the influence of free convection due to *compositionally induced density variations* in interdiffusion composition profiles.

To determine the interdiffusion coefficients accurately, there are two possible approaches. One is to design experiments in which the effect of free convection is suppressed or reduced. The other is to develop a theory to correctly account for the presence of free convection in interdiffusion.

Much of the effort in the past has followed the first approach. For ground based experiments, the obvious way to reduce the influence of gravity is to have the density increase in the direction of gravity. However, this does not completely eliminate the effect of the potential energy on the composition profiles. For example, in equilibrium, the composition will not be uniform - the denser component will be segregated at the bottom. Another method makes use of capillary tubes [1] to contain the two liquids of differing compositions relying on capillary forces to counteract free convection. Frischat et al [2] have recently shown this method to be problematic due to the variation in the values of interfacial tension (between liquid and the capillary surface) with liquid composition. Further, this method does not always work in ternary or higher component systems because an initially stable system (with density increasing along the direction of gravity) may become unstable at later times by compositional induced density changes. A third method uses complex experimental set ups to simulate zero gravity conditions in ground based experiments [3]. These methods, because of their inherent complexity (especially in the case of high temperature melts) are not suitable for generating experimental data on diffusion coefficients in a large number of systems. It is, therefore, desirable to follow the second approach and develop analytical schemes for taking into account the presence of free convection in simple experimental designs (like an infinite couple) which can be conveniently performed in most laboratories. This forms the motivation for this research program.

*Objectives:*

The objective of this research program is to provide a detailed understanding of the influence of free convection during interdiffusion. More specifically, the program aims:

a) to develop theoretical procedures for the evaluation of the interdiffusion coefficients from infinite couple experiments taking into account the presence of free convection, and b) to test the validity of these theoretical procedures by applying them to measured composition fields obtained in ground based experiments in a suitably chosen controlled-viscosity, isothermal, and isobaric binary liquid (or supercooled liquid) system and comparing the computed diffusion coefficient values with the corresponding values obtained in identical experiments in microgravity conditions where free convection is absent.

*Relevance to Microgravity:*

Free convection makes the interpretation of interdiffusion experimental results in liquid and supercooled liquid systems difficult. Temperature induced free convection can be eliminated by conducting the experiments isothermally. However, density variations as a result of compositional changes cannot be eliminated in a diffusing system. If the measurements of the diffusion coefficients have to be made in systems in which compositionally induced density variations are large, then a microgravity environment is most desirable for measurement of interdiffusion coefficients.

### *Review of Relevant Research:*

Because of the importance of interdiffusion in the processing of materials, a large amount of effort has been invested over several decades to measure the interdiffusion coefficients in various kinds of materials, and the progress has been summarized in many excellent reviews [4,5]. Diffusion coefficients are generally determined by analyzing the measured isothermal and isobaric evolution of a step composition profile. This configuration is known as an 'infinite couple' provided the end compositions are not perturbed by diffusion. The resulting composition fields are typically measured most conveniently by an Electron Microprobe Analyzer [6]. While the experimental procedure is straight forward, the analysis of the measured composition profiles for the purpose of extracting the diffusion coefficients is not because a) the interdiffusion coefficients are composition dependent, b) there is, in general, a volume change in the system upon diffusion, and c) free convection is present in liquid systems. The first two effects have been well studied as they are also present in solid systems where much interdiffusion work has been reported. For example, procedures, extending the Matano analysis (a technique for extracting the composition dependent values of the interdiffusion coefficient from measured composition profile), are available to account for volume changes [7]. However, there does not exist a procedure to account for free convection effects which are always present in fluid systems. Much of the previous work on interdiffusion in liquids and supercooled liquids has been analyzed under the assumption of absence of free convection.

Presence of free convection in interdiffusion experiments has been recognized by several investigators [1,2,3]. Most efforts have been directed at designing experiments to reduce the presence of free convection. Hunold and Bruckner [1] used the capillary method to avoid natural convection in glass melts during interdiffusion experiments. To further reduce natural convection, glass of higher density was always placed in the lower part of the capillary. Herr and Frischat [3] have also used the capillary method to study interdiffusion in  $\text{Na}_2\text{O-Rb}_2\text{O-SiO}_2$  melts. Up to  $1000^\circ\text{C}$ , no influence of convection was observed. Above  $1000^\circ\text{C}$ , they observed that that composition contours were no longer planar. In a later publication, Frischat and coworkers [2] point out the adverse influence of variation of the interfacial tension values between the two melts and the surface of the capillary tube (e.g., the contact angle at the interface is not  $90^\circ$  with respect to the tube wall causing the interface to be nonplanar).

### *Description of the Research Program:*

The research under this program is being carried out along two parallel but intertwining paths. Fluid dynamical modeling of interdiffusion in presence of free convection constitutes one path. The goal of this part is to develop a procedure (analytic if possible and numerical if necessary) to calculate the values of the composition dependent interdiffusion coefficients from composition profiles obtained in infinite couples (with vertical and horizontal orientations) taking account of the presence of natural convection. The other path of the research program consists of experimental studies of binary interdiffusion under isothermal isobaric conditions free from fluid

dynamic instabilities. Experiments will be carried out both in conditions of strong free convection and in conditions of weak free convection. These experimental results will be analyzed for interdiffusion coefficients using the procedure developed in the modeling studies. Comparison of the results under conditions of weak and strong free convection will provide a rigorous test of the developed procedure. At some time in the future, it is hoped that interdiffusion experiments will be performed in microgravity environment where compositionally induced free convection is absent. These experiments will provide the true values of the interdiffusion coefficients in the chosen system.

*Fluid dynamic modeling of interdiffusion in the presence of free convection:*

There are essentially four equations that govern the evolution of an isothermal binary diffusing system. The first is the continuity equation (i.e., equation for total mass balance):

$$\partial\rho/\partial t + \nabla \cdot (\rho\mathbf{V}) = 0 \quad (1)$$

where  $\rho$  is the total density and  $\mathbf{V}$  is the mass average velocity. The second is the diffusion equation (written for component A):

$$\partial\rho_A/\partial t + \nabla \cdot (\rho_A\mathbf{V}) = \nabla \cdot (D \nabla\rho_A) \quad (2)$$

where  $D$  is the interdiffusion coefficient, and  $\rho_A$  is the mass density of component A. The third is the momentum balance equation. It governs the evolution of the three components of the mass average velocity  $\mathbf{V}$ .

$$\rho [\partial\mathbf{V}/\partial t + \mathbf{V} \cdot (\nabla\mathbf{V})] = -\nabla p + \mu\nabla^2\mathbf{V} + \rho \mathbf{g} \quad (3)$$

Here  $p$  is the pressure,  $\mu$  is the shear viscosity, and  $\mathbf{g}$  is the acceleration due to gravity. The fourth equation is the equation of state for the system:

$$\rho = \rho(T, p, \rho_A)$$

The following approximation can be used for the equation of state for a condensed system:

$$\rho = \rho_0 + (\partial\rho/\partial\rho_A)_0 (\rho_A - \rho_{A0}) + (\partial\rho/\partial p)_0 (p - p_0) \quad (4)$$

Since we are interested in interdiffusion in an isothermal system, the energy balance equation can be ignored. The main problem in solving these four equations for the four unknowns ( $\rho$ ,  $\rho_A$ ,  $p$ , and  $\mathbf{V}$ ) lies in the fact that this system of equations involves non-linear coupled partial differential equations.

The 'infinite' diffusion couple will be in the shape of a cylinder (Radius, R) and of finite length (2L) along the axis. The initial composition profile will be a step function in the axial direction (the x-direction). Vanishing of the flux will be imposed as a condition at all boundaries of the cylinder reflecting their closed nature. The velocities (tangential as well as normal components) will be taken as zero at the boundaries.

It is useful to put the governing equations in a dimensionless form. To do so, lengths are normalized by radius R. Time is made dimensionless by scaling it with  $R^2/D$ . The mass densities are scaled by the density difference,  $\Delta\rho$ , for the two end compositions. The velocities are scaled by U which is given by:

$$U = g \Delta\rho (R \sin \theta)^2 / (\rho_0 \nu) \quad (5)$$

Here  $\nu$  is the kinematic viscosity,  $\theta$  is the orientation of the cylinder axis with respect to the vertical direction, and  $\rho_0$  is the density of the average composition. Under these conditions, the Rayleigh number Ra (which is the product of Grashof and Schmidt numbers) is a measure of the influence of free convection in the interdiffusion process:

$$Ra = U R / D \quad (6)$$

For horizontal orientation ( $\theta = 90$ ) Ra is much larger than 1 for typical supercooled viscous liquids [8], indicating that the free convection is not negligible even in highly viscous liquids.

#### *Experimental program:*

To keep the experiments and the theoretical analysis simple, diffusion will be studied isothermally. This will also eliminate temperature induced free convection. In an isothermal system, free convection can still occur due to compositionally induced density changes (the effect which we are investigating) and the undesired Marangoni effect (capillary induced free convection) due to the variation of surface tension with composition. This capillary induced flow can be eliminated by choosing a system where the surface tension does not vary with composition. However, this is possible only with very few systems in limited temperature and composition ranges. A better approach is to eliminate free surfaces by covering them with inert films. This can be used with any system and will be used in our experiments.

Since the main objective is to understand the role of free convection in interdiffusion, a binary system will be chosen as this is the simplest multicomponent system. Higher component systems involve the complexity of having many diffusion coefficients. It is hoped that sometime in future, after the theory is validated for the binary system, experiments will be proposed in ternary systems.

After diffusion treatment, the entire two dimensional composition field of an infinite couple will be measured by a technique such as the Electron Microprobe Analyzer. Simple liquids are not suitable for this purpose since composition profiles do not remain frozen at room temperature. On the other hand, solid systems are also not suitable for this purpose since they do not exhibit effects of free convection. Glasses, which are solid at room temperature and supercooled liquids at temperatures above their glass transition temperatures, are best candidates for our experiments.

Because of these considerations, we have chosen to use the PbO - SiO<sub>2</sub> system. This system offers the following advantages:

- a) a large single phase liquid field at temperatures above 765°C.
- b) a large variation of density with respect to change in composition [8].
- c) relative ease of measurement of composition profiles using an Electron Microprobe Analyzer.

*References:*

1. K. Hunold and R. Bruckner, *Glasstechn. Ber.*, 53, 207, (1980).
2. M. Braedt and G. H. Frischat, *J. Am. Ceram. Soc.*, 67, C-54, (1984)
3. M. Meier and G. H. Frischat, *Phys. and Chem. of Glasses*, 34, 71, (1993)
4. J. Philibert, "Atom movements: diffusion and mass transport in solids", *Les Editions de Physique*, (1991).
5. P. K. Gupta and A. R. Cooper, *Physica*. 54, 39, (1971).
6. J. Ganguly, R. Bhattacharya, and S. Chakraborty, *Am. Mineralogist*, 73, 901, (1988).
7. F. J. J. van Loo, *Acta Met.* 18, 1107, (1970).
8. N. P. Bansal and R. H. Doremus, *Handbook of Glass Properties*, Academic Press, (1986).